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Physics Procedia 48 (2013) 73 – 80

Physics Procedia

The XIII International Conference on the Physics of Non-Crystalline Solids

Viscosity and structure of lithium sodium borosilicate glasses

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Abstract

Viscosity and structure of sodium borosilicate glass doped with Li_2O were investigated by the rotating crucible viscometer and Fourier infrared spectrum. The melting temperature and activation energy for viscous flow of the studied melt were derived on the basis of Arrhenius equation, in order to reveal the effects of Li_2O substitution on the behavior of sodium borosilicate glass. As expected, introduction of Li_2O decreases the viscosity of elevated temperature melt, however, the results develop in the opposite direction when the concentration of Li_2O is over 1.00 mol. This abnormal phenomenon can be explained in terms of the high ionic field of Li_2O and the proportions of $[BO_3]$ and $[BO_4]$. As the increase of Li_2O, the boosting of the peak which is located about 1400 cm^{-1} due to the asymmetric stretching relaxation of B-O bond of $[BO_3]$ proves the decrease of free oxygen.

Keywords: Borosilicate glass; Li_2O; viscosity; structure; polarization effect;

1. Introduction

Borosilicate glasses with low alkali oxides, incorporated with outstanding thermal properties, excellent chemical stability and superior optical transmittance, are used for many applications such as optical glasses, oven wares, primary packing materials for pharmaceutical[1]. As a traditional industry, it is a fundamental

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doi:10.1016/j.phpro.2013.07.012

work to study high temperature physical properties, such as chinaware, processing of cement and glass melting[2]. In addition to controlling the ease of glass formation, viscosity is also important in managing the process of fining, forming and annealing [3]. Many effective works have been carried out in this field, and have obtained abundant data and patterns, involving soda-lime-silicate glass[4-6], calcium aluminosilicate glass[7,8]and sodium borophosphate glass[9]. However, in the related literature as far as we can found, accurate viscosity measurements of alkali borosilicate glasses or melts are still scarce. This lack of data is especially unfortunate because of the potentially wide applications of borosilicate glasses adopted with float process.

Park etc [10] predict that Li_2O additions up to 2wt pct were effective in decreasing the viscosity of calcium silicate melts containing 12wt pct Na_2O, but the effect was comparatively negligible above 2wt pct. The similar results have been reported by Wen[11], and was explained in terms of the network modification of the molten slag by free oxygen ions (O^{2-}) supplied by Li_2O. However, the systematic works on how effective of Li_2O substitute on viscosity and workability have not been promoted in the borosilicate glass system. In this paper, at the fixed concentration of boric acid and silica, the effect of Li_2O substituting sodium oxide on viscosity and workability was discussed.

The viscous properties and structure of melts closely associated. In general, changes in composition which reduce crossing-linking of the glass structure reduce the viscosity, while those which increase connectivity increase the viscosity. The structure of alkali borate and borosilicate glasses has been widely investigated, mainly via NMR analyses of ^{11}B, ^{23}Na and ^{29}Si. An original model had been proposed in 1970s by Yun and Bray[12]. The composition-related structural parameters K and R were quoted, while the ratios $K=[SiO_2]/[B_2O_3]$, $R=[Na_2O]/[B_2O_3]$ (where $[\cdot]\equiv$mol%). However, some recent publications [13-15] have shown that the borate and silica networks were randomly mixed than was assumed in [12,16]. Mixed alkali borosilicate glasses show a complex relationship between composition and structure[17]. Specifically, the sequence of polymerization of the silicate network and boron coordination is strongly dependent on glass composition. The differences in the free oxygen numbers and ionic field directly lead to variation of microstructure. The effect of Li_2O substitution on the strength of Si-O bonding and fraction of $[BO_3]$ and $[BO_4]$ were investigated.

2. Experimental

Glasses with compositions (81.00 SiO_2, 12.00 B_2O_3, (6.00-x) Na_2O, 0.50 CaO, 0.50 Al_2O_3, x Li_2O, expressed in mol%) were prepared using acid-washed quartz sand, and H_3BO_3, Na_2CO_3, and Li_2CO_3, of reagent grade, while x represents the substitution of moles of Li_2O in increments of 0.50 mol until 2.00mol. The batches were mixed well and melted for 3h in corundum crucibles in an open-air furnace at 1620 ^oC. Molten glasses were quenched in a few seconds from high temperature by dipping the bottom of the crucible into pure water. And then the glassy particles were dried for viscosity measurements. The glass samples were labeled with a short symbol from LN-0 to LN-4, where the LN-0 indicates the sodium borosilicate glass without Li_2O substitution. LN-1 to LN-4 increase with 0.50 mol of Li_2O at each level, respectively.

The viscosity of elevated temperature was measured with a rotating crucible viscometer (Orton RSV 1600). About 220 g of glass frit was added into a platinum crucible and placed into the furnace set at 1580 ^oC. To accurately control the process of measurement, the thermocouple was set above the melt level at a high temperature. The viscometer was calibrated for three times with a standard glass SRM717a (NIST selling) before testing. The standard measurement error is less than 0.05 log units. The infrared spectra of glasses were recorded at room temperature using KBr disc technique. A Nexus FTIR spectrometer was used to obtain the spectra in a wave number range between 400 and 4000 cm^{-1}. The dark current noise and background of the infrared spectra were corrected by the two-point baseline

correction. In order to eliminate the effect of the concentration of the powder sample present in the KBr disc, such normalization was essential.

3. Result and discussions

3.1. Elevated temperature viscosity

The viscosity data of measured samples shown in the Fig. 1 denoted the dependence between the viscosity and temperature. As the temperature reduced, the smaller anionic groups tend to polymerize for more complicated and larger groups, which resulted in the sharp increase in the viscosity. The viscous variations of Li_2O substitution depended on the content of Li_2O and temperature, as Fig. 1 plotted, and could be discussed in two temperature range.

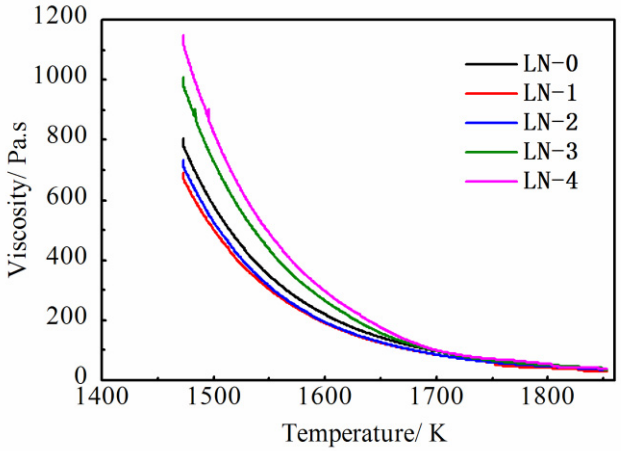

Fig. 1 Viscosity of sodium borosilicate glasses with respect to Li_2O substitution from 1473K to 1853 K

In the measured temperature range of 1473K and 1700K, the viscosity presents a minimum value when the substitution content is 0.50 mol. The larger content of Li_2O would rapidly increase the viscosity, ultimately causing the higher viscosity than sodium borosilicate melt. The result can be explained that Li_2O is one of the high cationic field oxides. The cationic field of Li^+ is equal to 1.65, which is more than as three times as the value of Na^+. The existent of small content Li_2O would affect the surroundings of Si-O, and then make significant influences in the bonding strength and integrity of the glass microstructure based on $[SiO_4]$. Specifically, not only Li_2O can provide free oxygen to destroy the network of $[SiO_4]$, but also make a dent in the bonding strength of ≡Si-O←R(R means monovalent cation) by the function of anti-polarization. The higher cationic field is, the more obvious the effect represents. The decline of viscosity for LN-1 is known to be due to the main effect of anti-polarization. However, as to the high Li_2O composition, the decisive effect of polymerization in stead of anti-polarization directly leads to the increase of viscosity.

In the evaluated temperature of above 1785K, all melts doped with various Li_2O content present lower viscosity than that of sodium borosilicate glass, just plotted in the Fig. 2. This interest phenomenon indicates the slight difference between the function of Li_2O in the various temperature ranges. On the one hand, Li_2O decreases the connectivity of network with the aid of high cationic field strength of Li^+ in the high temperature

range; on the other hand, high concentration of Li^+ is likely to draw the anionic groups to its side in the low temperature. The two effects which are provided above decide the variations of viscosity.

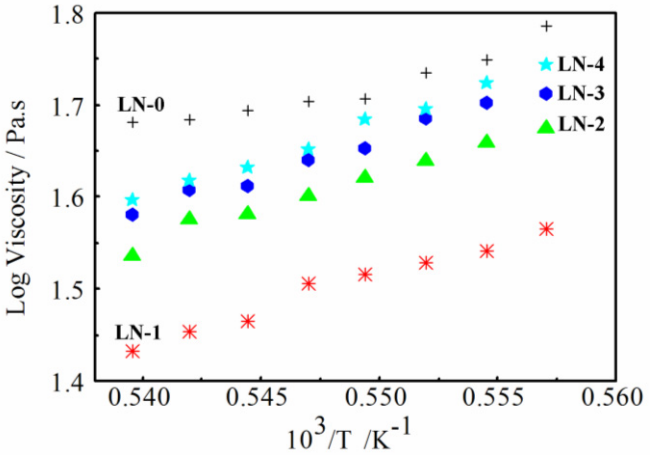

Fig. 2 Detailed viscosity at elevated temperature above 1785K of sodium borosilicate and sodium lithium borosilicate glasses

As we known, melts at high temperature range approximately obey Arrhenius law. The equation is expressed as 3-1. It is assume that viscosity is a thermally activated process with constant activation energy, although the supposition is available limited in narrow range at elevated temperature [18].

$$\mathrm{Log}\eta = A + B/T \qquad 3\text{-}1$$

(Where Log η means the logarithm of viscosity, A is pre-exponential constant, B is equal to ΔE_η/2.3RT, ΔE_η means activation energy, R is gas constant, T is the absolute temperature.)

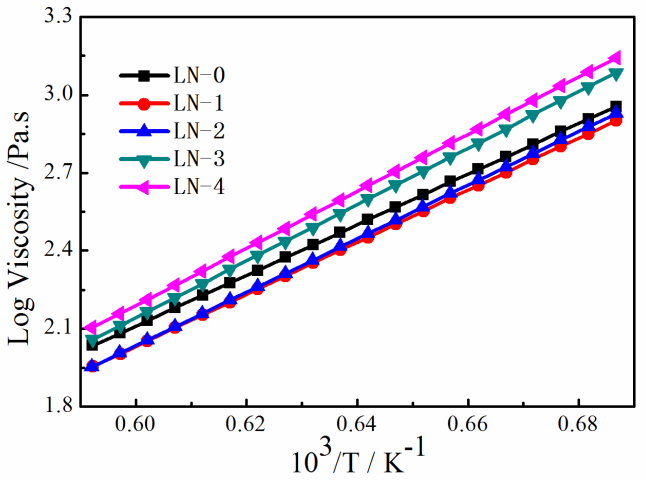

Fig. 3 Approximately linear relationship of log viscosity and 10^3/T for glasses with different Li_2O substitution at high temperature

Directly employing the equation 3-1, the dependence of viscosity on temperature was shown in Fig. 3. In the log viscosity range of 2 and 3, the linear relation between Log viscosity and 1000/T was satisfactory observed, however, the slopes of the straight line behaved obvious diversity. The fitted results were listed in

the Table 1, where the theoretical melting temperature Tm is defined as temperature at which η=10 Pa.s. Since this temperature is not a truly a melting point, but rather simply a processing temperature, the term practical melting temperature should be used to distinguish between the true melting points of crystals and a reference viscosity which is based entirely on curve for viscosity as a function of temperature[19]. The Tm of all samples doped Li_2O are lower than the base sample LN-1, and the substitution of 1.00 mol present the most effective in the lowing the theoretical melting temperature calculated from Arrhenius law. The tendency of activation energy roughly changes approximate consistent with viscosity, and it is necessary to research the development in the dependence of viscosity on activation energy in the future. Contributing to the excellent depolymerization and anti-polarization at high temperature, the addition of Li_2O decreases the theoretical Tm.

Table 1 Arrhenius parameter A, activation energy E_η and melting point T_m of glasses

Samples	A	B	E_η(KJ .mol^{-1})	T_m(^{o}C)
LN -0	-3.95	10.08	193.03	1763.21
LN -1	-3.96	9.99	191.31	1740.96
LN -2	-4.12	10.26	196.48	1730.76
LN -3	-4.43	10.94	209.50	1741.58
LN -4	-4.49	11.12	212.95	1752.35

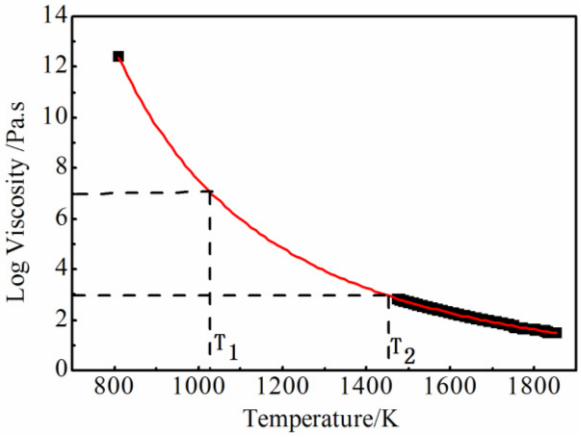

Fig. 4 Fitted curves of LN-1 applied AM model describing the dependence of viscosity on temperature between Tg and 1853K.

3.2. Workability

Above Tg, the dependence of viscosity on temperature in these systems often deviates strongly from the simple activated (or Arrhenius) behavior [20]. Empirical VFT model [21-23], AG model [24], AM model [25-27] and Mauro model [28] were proposed, every model was formed with different unique advantages in divergent glass systems or temperature range. It is unscientific and opinionated to describe which kind of model is the most accurate [29]. Unfortunately, the viscosity data of low temperature above Tg are hardly obtained during the laboratory conditions, but under we simply employ the only data point in the low temperature range, which is $\eta_{Tg}=10^{12.4}$ Pa.s. Tg is measured by thermal expansion testing. Fig. 4 illustrates the fitted curves of LN-1 as examples applied AM equation. All the AM fitted parameters of individual samples are listed in the Table 2, including the characteristic temperature valve of $\eta_{T1}=10^7$ Pa s, $\eta_{T2}=10^3$ Pa s and

η_{Tm}=10 Pa s.

The workability of melt weighing the speed of viscous variation on temperature is also one of the important rheologic properties, influencing the selection of technology of glass forming, etc. In the Table 2, $\eta_{T2}=10^3$ Pa.s, T_2 is called operation temperature. Another parameter T_1 matches the viscosity of 10^7 Pa.s. The temperature difference of T_1 and T_2 is used to roughly contrast the workability of samples. The results reveal that Li_2O generally increase the workability of sodium borosilicate melt, although the difference of LN-1 presents a litter abnormal. Differed with Na_2O, Li_2O present the effect of gathering anionic polymer and compact the microstructure because of high cationic field. With the increase of Li_2O substitution content, the accumulation effect represent more obviously, then causing the viscosity of low temperature increase. The increase of ΔT means the elongation of workability. The regulation of Tm calculated from AM model is similar to the result of Arrhenius Law; however, there are some differences between the values which come from the derivation process of models.

Table 2 AM fitted paramates of A, B(Tg) and friability index c, characteristic temperature T_1, T_2 and Tm referring to the viscosity of 10^7, 10^3 and 10 Pa.s, respectively.

Samples	A	B(Tg)/K	c	T_1/K	T_2/K	ΔT	T_m/°C
LN-0	-0.47	823.67	2.24	1035.39	1458.01	422.62	1866.21
LN-1	-0.58	807.13	2.22	1027.82	1450.37	422.55	1781.84
LN-2	-0.46	799.83	2.23	1024.06	1450.38	426.32	1818.84
LN-3	-1.07	792.80	1.94	1030.83	1469.92	439.09	1776.56
LN-4	-1.42	787.65	1.80	1033.08	1472.93	439.85	1766.86

3.3. Structure of lithium sodium borosilicate glasses

The compositional dependence of the viscosity of glass forming melts is closely related to the connectivity of the structure. As Fig. 5 depicted, intense absorption bands appear in the regions around 400 and 1600 cm^{-1}, and the FTIR spectra of five samples are similar. The peak located at about 470cm^{-1} is assigned to the bending vibration of silicate network. The bending vibration of $[BO_3]$ is expressed in about 700 cm^{-1}. The peak at 800 cm^{-1} is due to the symmetrical stretching vibration of Si-O-Si. The most complicated peak is located between 900cm^{-1} and 1300 cm^{-1}, which is due to the overlapping stretching vibration of Si-O-Si, $[BO_4]$ and mixed Si-O-B. The last peak is the 1300-1500 cm^{-1}, which is attributed to the asymmetric stretching relaxation of B-O bond of $[BO_3]$ units[30].

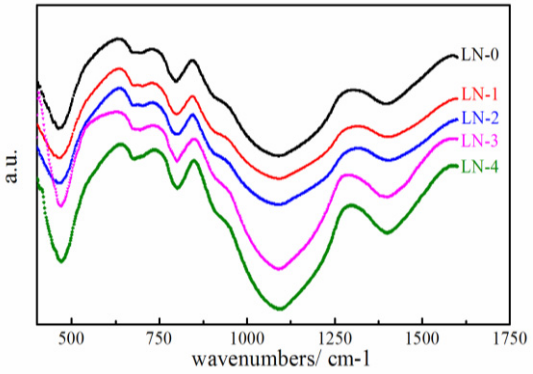

Fig. 5 infrared spectra of sodium borosilicate glass and lithium sodium borosilicate glasses

Fig. 5 shows that with the increase of Li_2O content there is no change in the shape and location of the spectra of LN-0, LN-1 and LN-2. The structure of three samples is similar to an extent. Unfortunately, and it is difficult to distinguish the slight structure modification from FTIR spectra. However, for LN-3 and LN-4, the broad peak between 900 and 1300 cm^{-1} become sharp and intense, which is due to the accumulation effect of Li_2O. The structure of borosilicate glasses is compacted for the substitution of more than 1.00 mol% Li_2O. Further more, the peak at 1400 cm^{-1} assigned to $[BO_3]$ stretching vibration become stronger than LN-0. The result can be explained as the ability of providing free oxygen of Li_2O is lower than that of Na_2O, causing the percentage of $[BO_3]$ decreased.

In a word, the messages obtained from FTIR spectra are limited, due to the overlapping contributions of silicate and borate groups. The measurement of structure would employ new technique with high resolution, for example MAR-NMR.

4. Conclusion

The effect of Li_2O substitution on the viscosity was correlated directly with the glass structure as revealed by FTIR of glass. Although the ability of Li_2O on providing free oxygen is weaker than Na_2O, the polarization effect is stronger attributed to its high cationic field which weaken the bonding strength of Si-O-Si. Slight substitution contributes to decrease the viscosity, and the viscosity reaches the minimum at the content of 1.00 mol Li_2O. In the low temperature range, Li_2O associate the anion units resolved and make the viscosity increase. More accurate measure and deep analysis have to be done on the fitted dependence of viscosity on temperature and the FTIR spectra on the range of 900-1200 cm^{-1} in the future work.

Acknowledgements

The authors thank Shahe Glass Design & Research Institution for samples test of viscosity. The authors are also grateful for the helpful comments from the reviewers.

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